

reaction channel or channels. The use of a flow-by catalyst configuration can create an advantageous capacity/pressure drop relationship. In a flow-by catalyst configuration, fluid preferably flows in a gap adjacent to a porous insert or past a wall coating of catalyst that contacts the microchannel wall (preferably the microchannel wall that contacts the catalyst is in direct thermal contact with a heat exchanger (preferably a microchannel heat exchanger), and in some embodiments a coolant stream contacts the opposite side of the wall that contacts the catalyst).

[0082] Metal Aluminide Layer

[0083] In some embodiments of the invention, at least a portion of at least one interior wall of a microchannel apparatus (preferably a microreactor) is coated with a layer of a metal aluminide (preferably nickel aluminide (NiAl)). It has been surprisingly discovered that an alumina wall coating formed by oxidizing a metal aluminide (NiAl in the examples) coating provides superior corrosion resistance as compared to either thermally grown oxide layer (grown from the substrate without forming an aluminide) or a solution deposited alumina layer. It is believed that exceptionally uniform and dense coatings result from solid state reaction of aluminum deposited at the surface from the gas phase and nickel diffusing out from the substrate towards the surface. In addition, nickel may be plated onto a metal that is not rich in nickel, such as stainless steel, to create a reactive surface for the aluminidization process. Nickel aluminide could also be deposited by supplying both Al and Ni precursors in the vapor phase concurrently or as a mixture. In a related aspect, a catalyst or catalyst intermediate is formed on substrates having such a nickel aluminide surface. Of course, the invention also includes methods of making catalysts or microchannel apparatus comprising coating a substrate (preferably a Ni-based alloy) with chemically vapor deposited aluminum that is simultaneously and/or subsequently converted to an aluminide (such as NiAl).

[0084] A NiAl layer can be formed by exposing a Ni-based alloy to AlCl_3 and H_2 at high temperature, preferably at least 700°C ., in some embodiments 900 to 1200°C . Aluminum is deposited at the surface as a result of the reaction between AlCl_3 and H_2 . At temperature, Ni from the substrate would diffuse towards the surface and react with the aluminum to form a surface layer of nickel aluminide. The Ni source could be Ni in a Ni-based alloy substrate, an electrolytically plated Ni layer or a vapor deposited Ni layer that can be deposited over a substrate prior to aluminidization. It is believed that other metal aluminides (such as Co or Fe) could be formed under similar conditions.

[0085] Preferably, the aluminidization process is conducted with good control of flow to the device through a manifold. For example, good control can be obtained by passing flow into microchannels through a leak-free manifold. Preferably the aluminidization process is carried out at 100 Torr (2 pounds per square inch absolute, psia) to 35 psia (1800 Torr), more preferably between 400 Torr (8 psia) and 25 psia (1300 Torr).

[0086] In preferred embodiments, nickel aluminide contains 13 to 32% aluminum, more preferably 20 to 32%; and still more preferably consists essentially of beta-NiAl. If Al falls significantly below the 13% weight % level of the gamma-prime phase, it may be expected to negatively affect the quality of the thermally-grown alumina scale.

[0087] In some embodiments, the metal aluminide layer has a thickness of 1 to 100 micrometers; in some embodiments a thickness of 5 to 50 micrometers. In some embodiments, the aluminide layer is completely oxidized; however, this is generally not preferred.

[0088] The metal surface upon which the metal aluminide is formed is preferably substantially free of oxides. Optionally the surface can be cleaned, polished, or otherwise treated to remove such oxides if any are present.

[0089] A reactor can be formed by a catalyst that is disposed as a coating on an interior wall (where the walls can be simple walls or shaped walls). Alternatively, or in addition, inserts such as fins, plates, wires, meshes, or foams can be inserted within a channel. These inserts can provide additional surface area and effect flow characteristics. An aluminidization process can be used to fix inserts onto a wall of a device (such as a reactor); the resulting aluminide layer fills some voids and greatly improves thermal conduction between the insert and device wall (such as reactor wall).

[0090] Thermally Grown Oxide

[0091] Metal aluminide or more preferably NiAl layer, is heated in the presence of oxygen or other oxidant to grow a layer of aluminum oxide. It was surprisingly discovered that when the surface was first heated to the treatment temperature in the absence of O_2 or other oxidant, prior to growth of the oxide layer, a significantly improved oxide coating resulted. The oxide layer grown during heating the surface to the treatment temperature in the presence of oxygen exhibited spalling while the layer grown by heating the surface from ambient temperature to the treatment temperature in the absence of oxygen did not. Oxygen can be substantially excluded from the heat up step of the heat treatment process.

[0092] A convenient and preferred method of excluding oxygen from the surface while heating the surface from ambient temperature to treatment temperature involves exposure to hydrogen. The hydrogen effectively reduces the oxidizing power of the atmosphere during heat up to prevent premature growth of the oxide scale. Other gases that reduce the oxidizing power of the gas, such as NH_3 , CO, CH_4 , hydrocarbons, or the like, or some combination of these could also be used. All of these reducing gases could be used in combination with inert gases such as N_2 , He, Ar, or other inert gases, or combinations of inert gases.

[0093] The oxide layer is then preferentially formed by exposing the surface to an oxidizing atmosphere at or within 100°C . of the heat treatment temperature. The oxidizing gas could be air, diluted air, oxygen, CO_2 , steam or any mixture of these gases or other gases that have substantial oxidizing power, with or without an inert diluent. The inert diluent could be inert gases such as N_2 , He, Ar, or other inert gases, or combinations of inert gases. The temperature of oxide growth is at least 500°C ., preferably at least 650°C . The surface can be exposed to the treatment condition in stages of different temperatures, different oxidizing powers, or both. For example, the surface could be treated at 650°C . for a time and then heated to 1000°C . and kept at 1000°C . for an additional time. Such controlled and staged surface treatment can generate a surface structure of a desired morphology, crystalline phase and composition.

[0094] Superior oxide coatings result from preheating to about 1000°C . (in some embodiments at least 900°C .)